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A Comparison of the Chlorinated Hydrocarbon Content of Surface and Subsurface Samples in the York River, Virginia

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A COMPARISON OF THE CHLORINATED HYDROCARBON CONTENT OF SURFACE AND SUBSURFACE SAMPLES IN THE YORK RIVER, VIRGINIA

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ABSTRACT

A comparison of the concentrations of chlorinated hydrocarbons was made from surface slick and subsurface samples from the York River, Virginia. The surface slick samples were taken by a drum skimmer; the subsurface samples were taken by immersion of a sample bottle to 1 meter.

Results showed DDT and PCB (Aroclor 1254) slick concentrations in the range of 0-60 ppt (parts per trillion weight-weight). These concentrations were much below those found by Seba and Corcoran (1969) in slicks in the Biscayne Bay, Florida. The concentrations of chlorinated hydrocarbons from the present study were generally higher in the surface than in the subsurface samples. The probable mechanisms by which these substances were concentrated in slicks were discussed.

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INTRODUCTION

There has been much concern recently about the pollution of our environment by chlorinated hydrocarbons. Seba and Corcoran (1969) showed that surface slicks have the ability to concentrate chlorinated hydrocarbon pesticides. If more information were available on the ability to concentrate chlorinated hydrocarbons, slicks could be used to indicate the amount and source of inputs of these pollutants to our environment. In this study samples of surface slick and subsurface water (1 meter) of the York River were evaluated for their chlorinated hydrocarbon content to determine if the relatively high concentrations of these substances found in slicks sampled in heavily polluted Biscayne Bay (Seba and Corcoran, 1969) were universal. Information on the chlorinated hydrocarbon concentrating phenomenon of slicks is also presented and discussed.

Polychlorinated biphenyls (PCB) are another group of chlorinated hydrocarbon compounds that have become widely spread in the environment. They have a wide variety of industrial uses. Commercial preparations such as Monsanto Aroclor 1254 are mixtures of different chlorinated biphenyl compounds, with the last two digits of the name indicating

the percent weight chlorine. The exact composition of these mixtures is not available, but according to mass spectra the components of Aroclor 1254 are mostly tetra, penta, hexa, and heptachlorobiphenyls (Koeman and van Genderen, 1969). Some of the uses of Aroclor 1254 are the following: as a secondary plsaticizer to improve flame retardance and chemical resistance of polyvinyl chloride, with ethylene vinyl acetate to make pressure sensitive adhesives, to enhance resistance, flame retardance, and the electrical insulating properties of chlorinated rubber, and as heat transfer fluids (Monsanto Technical Bulletin; Duke et al., 1970). PCB are concentrated by organisms, and are widely spread in the environment (Harvey et al., 1971). PCB in general seem to have less acute toxicity than DDT, but their sublethal effects are, as yet, poorly understood (Peakall and Lincer, 1970).

Parker and Barsom (1970) pointed out that there were no explanations of how DDT became so universally distributed. They expressed amazement that the surface microlayer had received so little attention as a possible reservoir for DDT and other similar substances. Seba and Corcoran (1969) sampled with bottles and found high chlorinated hydrocarbon pesticide concentrations in semi-permanent surface slicks in Biscayne Bay, Florida. They did not explain or postulate the mechanisms by which chlorinated hydrocarbons were concentrated in surface slicks.

These mechanisms are thoroughly discussed here because knowledge of these mechanisms could enable reseachers to assess the role of surface slicks in transporting and concentrating these substances. The results of this study are compared with Seba and Corcoran's to determine the universality of their findings.

SAMPLING METHODS AND MATERIALS

Surface and subsurface samples were collected from the York River at irregular intervals from November 1970 - November 1971. Slicks sampled were observed and classified as follows: (1) Light slick - capillary wave dampening under light winds (0-5 mph. estimated), (2) medium slick - (usually containing light debris), capillary wave dampening with winds estimated at 5-10 mph., (3) heavy slick - (usually containing much debris), capillary wave dampening with winds estimated at 10-15 mph. Non-slick surface and subsurface samples were taken for comparison of chlorinated hydrocarbon content with the different slick types.

Twelve liter surface samples were taken with a boat-mounted ceramic coated drum skimmer which was also used by Windsor (1972) in his analysis of surface films. The drum skimmer was built by NASA, Wallops Island Station. This apparatus avoided contamination while sampling, and samples were taken easily and quickly. When sampling, the boat was operated in the upcurrent direction to avoid collection of engine oils. Samples of the surface layer were collected in a stainless steel trough and drawn under vacuum into an 18 liter glass bottle. The sampling apparatus was washed with chloroform before each sampling day and flushed with new

sample at each station. All glassware was washed, rinsed with tap water (then distilled water), dried with acetone, and rinsed with petroleum ether before each use. Thus, only stainless steel, glass, and teflon contacted the sample. This prevented contamination of the sample by grease, oils, fats, etc., that might have had high chlorinated hydrocarbon concentrations.

The subsurface samples were taken by a swimmer who immersed an 18 liter glass bottle to approximately 1 meter and allowed it to fill to the 12 liter line.

EXPERIMENTAL

In the laboratory, the 12 liter sample was transferred from the sample bottle to a 20 liter glass carboy with a bottom drain stoppered with a clamped teflon tube. The sample bottle was washed three times with 250 ml of pesticide-pure petroleum ether and these washings were also added to the carboy. The carboy was stoppered and the contents shaken vigorously for 5 minutes; at the end of shaking the water layer had become cloudy. The sample was allowed to stand overnight in the carboy, and the next day the clear water layer was drained off through the bottom spigot and the ether portion was collected in a 2000 ml round bottom flask. Three grams of anhydrous Na_2SO_4 were added to remove the remaining water, and the sample was taken to dryness on a rotary evaporator. The sample was redissolved and transferred to a 50 ml beaker by three washings (15 ml each) of pesticide-pure petroleum ether. The petroleum ether was allowed to evaporate to a volume of about 0.5 ml. The 0.5 ml sample and two ether washings (1 ml each) of the 50 ml beaker were then added to a 3.0 ml centrifuge tube. The sample was then evaporated to 0.25 ml in a jet of prepurified nitrogen, spotted on thin layer plates, and de-

veloped in CCl_4 to the 10 cm line in a TLC chamber according to the procedure of Breidenbach et al. (1966). Silica gel on the plate from 2 cm to 10 cm (the area containing the chlorinated hydrocarbon pesticides and PCB) was scraped off and collected by a vacuum silica gel collection assembly. Chlorinated hydrocarbons adsorbed on the silica gel were eluted into a graduated centrifuge tube by 15 ml of 50% petroleum ether-acetone solution. The samples were again reduced to 1.0 ml in a jet of prepurified nitrogen and analyzed by a Perkin-Elmer 900 gas chromatograph fitted with an electron capture detector. Two columns were used for sample analysis, one was 3% DC-200 on Varaport 30 80/100 mesh, the other was QF-1 on Chromosorb G/AW/DMCS 80/100 mesh. Identifications of PCB and DDT family pesticides were made by comparing retention times of sample peaks with the retention times of known standards on both columns.

The DDT content of samples could not be measured directly, because one polychlorinated biphenyl compound had an identical retention time as DDT and interfered with its analysis. Two injections of each sample were needed to determine the DDT content. The area of the DDT polychlorinated biphenyl peak was measured on the chromatograms of each sample. The sample was then reacted with an excess of methanolic KOH. Methanolic KOH dehydrochlorinated DDT to DDE, but did not react with the polychlorinated biphenyls. A portion of the reacted sample was then injected and the area

of the DDT peak on the resulting chromatogram was measured. The DDT concentration of the sample was determined by comparing the reduction in the DDT peak area with the area of a DDT peak of a known concentration standard. To check the efficiency of conversion of DDT to DDE by excess methanolic KOH a DDT standard was dehydrochlorinated in excess methanolic KOH. All measurable DDT was converted to DDE. This indicated that the sample peak left at the DDT position in the second chromatogram of the samples was a polychlorinated biphenyl which did not dehydrochlorinate in methanolic KOH.

Concentrations of PCB were determined by measuring the heights of four peaks that were not interfered with by members of the DDT family and comparing their peak heights with the four corresponding peak heights of a known concentration standard of Aroclor 1254.

Pesticide and PCB standards of known concentration were mixed into twelve liters distilled water, extracted with petroleum ether, and run through the procedures conducted on samples to provide information on extraction and procedure efficiencies. Twelve liters of distilled water were extracted and run through the procedure to serve as a blank. A 750 ml petroleum ether blank was evaporated in the rotary evaporator and was similarly treated. No interfering substances were found in the petroleum ether blank, but peaks corresponding to Aroclor 1254 were found in the distilled water at a concentration of 6 nanograms/liter.

These peak heights were subtracted from the pesticide and PCB standards to obtain procedure and extraction efficiencies. The efficiencies were: 50% for Aroclor 1254 (all peaks in same ratios as the standard), 6% for DDE, 20% for DDD, and 18% for DDT. The appropriate efficiencies were used for determining the original concentrations of PCB and DDT in the samples.

Similarities in the chemical structure of PCB and chlorinated hydrocarbon pesticides (especially the DDT family) caused extensive masking and interference of peaks when the samples were analysed on the gas chromatograph. Several methods for total separation of PCB and chlorinated hydrocarbon pesticides were tested in an attempt to obtain quantitative data on both groups. Although several researchers (Holden and Marsden, 1969: Reynolds, 1969) have claimed success in this separation, difficulties were well known and documented (Zitko, 1971). To date, no consistent and practical total separation of PCB and chlorinated hydrocarbon pesticides at low concentration levels (10^{-10} g/ul) has been established by this laboratory. Without total separation of chlorinated hydrocarbon pesticides and PCB the concentration estimates for PCB were less accurate and the concentration of some pesticides could not be evaluated.

Separations similar to Reynold's (1969) Florisil column separation of Aroclor 1254 and chlorinated hydrocarbon pesticides were tested and found to be unsatisfactory because of

solvent contamination and the variability of Florisil and pesticide-pure solvents. Volumes of 200 ml of hexane or 200 ml of 20% diethyl ether in hexane solution from the elution of the Florisil column in the Reynolds' procedure were concentrated to approximately 0.5 ml in order to analyze the small amounts of chlorinated hydrocarbons obtained in this study. Gas chromatographic peaks of contaminants interfering with chlorinated hydrocarbon analysis were observed from both the concentration of 200 ml pesticide standard hexane (Nanograde, Mallinckrodt), or 20% diethyl ether hexane solution to 0.5 ml. Unpredictable and incomplete elutions resulting from the variability of Florisil and the differing elution properties of pesticide grade solvents (Zitko, 1971) made Reynolds' separation technique further undesirable for this study.

The Holden and Marsden (1969) silica gel procedure for separating PCB and chlorinated hydrocarbon pesticides used smaller amounts of solvents and interfering peaks from solvent contamination concentration were thereby reduced. However, silica gel columns, like Florisil columns, varied in their elution properties. Two types of silica gel, different column loadings, and different silica gel deactivations (by shaking with distilled water for thirty minutes), were used in an attempt to separate Aroclor 1254 from DDT and DDD, but no consistent and reliable separation was found.

Thin layer chromatography procedures similar to Mulhern's (1968) for the separation and removal of organochlorine insecticides from thin layer plates were tested using Aroclor 1254 and a DDE, DDD, and DDT standard, but the separations were ineffective.

Differentiation and identification of PCB and chlorinated hydrocarbon pesticides in the samples by gas chromatographic analysis of nitrated sample extracts was not attempted because some of the PCB also nitrate and clear cut identifications could not be made (Reynolds, 1969).

The accuracy of PCB concentration measurements was difficult to determine and Richardson et al. (1971) have suggested that the quantification of PCB with any degree of accuracy was impossible. Accuracies of most PCB quantifications were questionable because individual chlorinated biphenyl compound standards were not available and the response of the electron capture detector varied for each compound. But Koeman and van Genderen (1970) showed that Aroclor 1254 was composed mostly of tetra-, penta-, hexa-, and heptachlorobiphenyls, and the electron capture detector response to these compounds did not vary by more than a factor of 2 (Zitko and Choi, 1971). The error in the accuracy of the PCB concentrations determined in this study was probably not more than 2 times the PCB concentrations shown on Table 2. In view of the relatively small concentrations of PCB found in this study, this error was not serious. However, the precision of the PCB measurements was important, because the concentrations

of PCB in the samples from this study were compared with each other and with the results of other works.

The DDT concentrations were not subject to the same accuracy errors as the PCB, because single compound standards of known concentration were available. If the concentration and composition of the DDT standard and the samples remained constant over the period of analysis then the only accuracy error in determining the DDT concentrations resulted from the indeterminate errors from repeated injections of the DDT standard and the sample. The indeterminate errors for PCB and DDT on Table 2 were determined from injections of DDT and PCB standards and of surface sample 1. The absolute deviations for the injections of standards and samples were calculated using

$$d = \left(\sum \left| X - \overline{X} \right|\right) / N$$

$\overline{X}$ = average conc.

N = number of inj.

The absolute deviations were used for calculating the total error in the result by

$$r = \pm\sqrt{a + b}$$

a = absolute deviation of std. conc. inj.

b = absolute deviation of sample conc. inj.

according to Kolthoff and Sandell (1952). The indeterminate error calculated was ± 5.8% for DDT, and ± 6.8% for PCB.

The degree that the results represented the PCB and DDT concentrations in slicks was also dependent on the pre-

cision of the sampling apparatus, and the precision of the extraction process. These errors were assumed to be similar for each sample because great care was taken to assure that each sample was treated identically throughout the procedure.

The accuracy of the DDT concentration measurements was probably good and dependent on indeterminate error. But difficulties in the quantification of PCB affect the accuracy of concentration determinations for these substances. Repeated injections of standards and of a sample showed that the DDT and PCB concentration determinations were reproducible. The concentrations shown on Table 2 probably well represent the concentrations of these substances in slicks for comparison purposes.

RESULTS

The DDT concentrations found in the samples from this study were similar to those found in water samples from western streams by other workers (Brown and Nishioka, 1967). Duke, Lowe, and Wilson (1970) showed that PCB (Aroclor 1254) concentrations could at times be great (275 parts per billion, weight-weight) due to the accidental introduction of these pollutants from industry, but they found values in the range of this studies data (100 parts per trillion, weight-weight, in Escambia River to nondetection in Escambia Bay) following correction of the 1254 leak.

A total chlorinated hydrocarbon count was determined for all the samples from this study. This count was the total peak height of all indentifiable chlorinated hydrecarbons in the chromatograms, and it was expressed in graph units. The chlorinated hydrocarbons were indentified by retention times. Procedure efficiencies were not used in the count calculations. This count was used for comparison of the chlorinated hydrocarbon content of surface and subsurface samples. The chlorinated hydrocarbon count was higher in surface than in subsurface samples in five of the seven transitory slicks, but only higher in the surface sample on one of the two dates that the semi-permanent slick was sampled (Table 1).

The reasons only small amounts of PCB and trace amounts of DDT were detected in transitory slick samples 8, 10, and 11 were unknown (Table 2). Since both surface and subsurface samples had low concentrations, it seemed likely that the chlorinated hydrocarbon input to the water surface was low before and during the time these samples were obtained. Data from these samples were not used in calculating the DDT and PCB concentrations for transitory slicks.

Only four of the transitory slick samples from this study had measurable concentrations of DDT. The DDT concentrations were higher in the surface than in the subsurface samples in all four cases (Table 2). The average DDT in these transitory slick samples was 36 ppt (parts per trillion, weight-weight). The average DDT from the corresponding subsurface samples was 13 ppt. Concentrations of PCB (Aroclor 1254) were higher in surface than in subsurface samples in three of these four samples (Table 2). The concentration of PCB from these samples averaged 31 ppt in the surface and 16 ppt in subsurface samples (Table 4). These results were similar to those of Seba and Corcoran (1969) who found 19 ppt total DDT in a transitory slick (S-7) in the main axis of the Florida current.

The concentration of DDT in surface samples was higher than the concentration in subsurface samples on both dates that the semi-permanent slicks were sampled. The DDT concentration in the surface samples averaged 27 ppt.

The corresponding subsurface samples averaged 16 ppt DDT. The PCB (Aroclor 1254) concentration was higher in the surface sample on one date and higher in the subsurface sample on the other date. PCB averaged 16 ppt in the surface samples and 12 ppt in the subsurface samples. The results of this study for semi- permanent slicks were much lower than Seba and Corcoran's (1969). They found 61 ppt to 3.469 ppb (parts per billion, weight-weight) DDT in semi-permanent slicks which were associated with the mouths of drainage canals in the Biscayne Bay. Corcoran (personal communication) reported that PCB were present in very low or nondetectable concentrations in their samples. They found 2-39 ppt Dieldrin and 5-34 ppt Aldrin in slick samples, but neither of these pesticides were detected in the present study.

Classification of slick type was ineffective for indicating the amount of chlorinated hydrocarbons in the surface samples (Table 1). This was not surprising because the age, composition, and the source of the slicks in this study were unknown.

DISCUSSION

The surface film is unique, being the interface between two environments. It is a free surface and a depository for such substances as oils, fatty acids, and hydrocarbons that are only slightly soluble in water. It is this last attribute which most concerns this study. Non-polar molecules such as chlorinated pesticides and PCB apparently tend to collect in the oil slick surface because they are more soluble there than in the water. Although Seba and Corcoran (1969) found high concentrations of chlorinated hydrocarbons in surface slicks, the role of surface slicks in concentrating and transporting chlorinated hydrocarbons is, as yet, poorly understood. The data from this study indicate that some concentrating mechanism for chlorinated hydrocarbons operates on slicks, and that there are differences in this mechanism for semi-permanent and transitory slicks. The chlorinated hydrocarbon concentrations found in this study are not as high as those found by Seba and Corcoran (1969), but this is probably a reflection of the extent of pollution in the different sampling areas. The probable mechanisms for the concentration of chlorinated hydrocarbons in surface slicks are discussed here.

The original chlorinated hydrocarbon content of the

slick material was assumed to be non-detectable, and the input of chlorinated hydrocarbons from organisms also taken in the samples was assumed to be low. Actually fish oil slicks could have had detectable chlorinated hydrocarbon concentrations in the starting material, but the original concentrations of these substances in petroleum oil slicks presumably would have been non-detectable. The assumption of low or non-detectable original chlorinated hydrocarbon concentrations for slicks seemed valid because boating and industry in the sampling area released petroleum oil slicks which probably constituted many or all of the slicks in this study. The samples from this study, like those of other workers (Seba and Corcoran, 1969) were not filtered because filtration would remove dust particles, organisms, and other debris and their adhering chlorinated hydrocarbons. Plankton could have concentrated chlorinated hydrocarbons and since some of these cells could have ruptured in the extraction process their chlorinated hydrocarbon content could have caused error in the results. But the assumption that the contribution of chlorinated hydrocarbons to our samples from organisms was low was probably valid because most of the samples were taken in cold weather when the concentration of organisms was low, and because the volumes of the organisms and their concentrations of chlorinated hydrocarbons were small compared with the amount of sample taken.

Seba and Corcoran (1969) reported chlorinated hydrocarbon pesticide concentrations up to 12.750 ppb (parts per

billion) in samples from semi-permanent slicks formed at the mouths of drainage canals in Biscayne Bay, Florida. These canals drain southwest Dade County. Heavy pesticide ues in the drainage area was the probable source of the pesticides found in their slicks. However, the method of transport of these pesticides from the point of application to the slick, and the possible mechanisms of concentration of these substances in slicks were not explained. Seawater taken at the same time as the samples generally had no detectable amount of pesticides. Samples 12 and 13, from the present study, were taken at a semi-permanent slick at the mouth of Queen's Creek which drains into the York River. These samples had lower DDT concentrations than the Biscayne Bay slicks (Seba and Corcoran, 1969). This was probably a result of the lower pesticide use in the drainage area of Queen's Creek. It seemed likely, in semi-permanent slicks that the pesticides were washed with soil particles, petroleum oil, and the other hydrocarbons and fats into drainage canals or creeks and were then carried to the large bodies of water.

The higher flow rates of the canal or creek would keep the soil particles, pesticides and droplets of slick material in suspension, but on reaching the larger bodies of water (with their reduced flow rates) the emulsion-suspension would start to separate. As the droplets of slick material floated upward through the water column they would collect the pesticides from the water soil suspension. This

upscrubbing would be a liquid-liquid extraction. The requirements for a successful liquid-liquid extraction are the following: the two liquids chosen are not miscible, the substance to be extracted is more soluble (usually much more soluble) in the added liquid, and that sufficient contact between the two liquids takes place. The upscrubbing of water by droplets of slick material fulfills all these requirements so the upward moving slick material would be expected to collect the chlorinated pesticides. The continuation of upscrubbing would result in a slick with higher chlorinated hydrocarbon pesticide content than the surrounding water.

Upscrubbing would have also collected PCB in their samples, but Seba and Corcoran (1969) found low levels of PCB. It is thus likely that these small concentrations were a result of a low PCB input in their area.

Some concentration of chlorinated hydrocarbons could occur from the water currents around and below the slick. The chlorinated hydrocarbons would tend to remain with the slick material because they are much more soluble in oils than in water (Hartung and Klinger, 1970). It is unlikely that this would be a major concentrating mechanism because contact between oil and water would be low (and the efficiency of the liquid extraction reduced) unless high flows exist around the slick. The high flow rates necessary to greatly increase the oil water contact (and thereby increase the chlorinated hydrocarbon transfer to the oil) would break

up and dissipate the slick.

The wave initiated down-mixing of slick material and its subsequent return to the slick could have also resulted in higher concentrations of chlorinated hydrocarbons in slicks. The droplets of down-mixed slick material would have extracted chlorinated hydrocarbons from the water a few inches to a few feet below the slick. This process would also have been a liquid-liquid extraction. Little is known about down-mixing of oil, but the author has observed (in a one foot chop sea) droplets of oil to a two foot depth under petroleum oil slicks. In higher seas the depth of down-mixing of oil droplets would have been increased. Some of the droplets, with their increased chlorinated hydrocarbon content, would have floated back to the slick and increased its chlorinated hydrocarbon concentration. The highest chlorinated hydrocarbon concentration observed in this study was found in a transitory slick which probably originated at the West Point pulp mill. If the estimation of the source of this slick was correct, it had traveled approximately 30 miles downstream. Most likely a portion of its chlorinated hydrocarbon content was obtained by the down-mixing and return mechanism.

Harvey et al., (1971) found DDT and PCB (Aroclor 1254) in open ocean organisms. He suggested that the primary method of transport of these substances to the open ocean was aeolian (personal communication). Surface slicks could also have inputs of chlorinated hydrocarbons from the air.

DDT was introduced to the atmosphere by aerial spraying for agricultural pests and mosquitoes, and was believed to be carried on dust particles (Harvey et al., 1971). PCB could enter the atmosphere as gases from the incineration of some plastics (Heath et al., 1970). Once in the atmosphere these substances could have settled with dust particles into slicks or entered them in rain. The input of chlorinated hydrocarbons to slicks from this method should have been directly related to the time and area of slick exposure. The addition of pesticides and PCB to slicks from the air could have been considerable when slicks have been exposed to the environment for long time periods as in semi-permanent slicks, or where extensive aerial spraying had been utilized, as in Dade County (Seba and Corcoran, 1969).

The data of this study indicated that the aerial input of DDT was not the primary method that increased the concentration of DDT in transitory slicks in the York River. Surface sample #4 was a petroleum oil slick that presumably started with a non-detectable chlorinated hydrocarbon concentration and was sampled a short time after originating from the American Oil pier. This sample with an exposure time of less than two hours, had 5 times the DDT concentration of the corresponding subsurface sample. If the aerial input of DDT was sufficient during the two hour exposure span to increase the DDT level of the slick in surface sample #4, from 0 to 26 ppt (parts per trillion, weight-weight), then the non-slick surface samples taken on

the same date in nearby locations should have also indicated this high aerial input. Since other samples taken on the same date (3 and 5) had approximately equal surface and subsurface DDT content, it seemed likely that some mechanism other than direct aerial input into slicks caused the higher DDT concentrations observed in surface sample #4. It was also apparent that the DDT concentrating mechanism could operate in a short time span.

In the four transitory slicks, where DDT concentrations were measurable, the DDT content of the surface sample was higher than the DDT content of the subsurface sample. The DDT concentration averaged 36 ppt (parts per trillion weight-weight) in surface samples and 13 ppt in subsurface samples (Table 2). PCB (Aroclor 1254) concentrations were measurable in seven transitory slick samples; four had higher PCB content in the surface sample. The average surface PCB (Aroclor 1254) concentration of the four samples (used for determining the average surface and subsurface concentrations above) was 31 ppt, the average PCB content of the four subsurface samples was 16 ppt. This indicated that DDT was more concentrated at the surface and that PCB (Aroclor 1254) were more uniformily distributed with depth.

Harvey et al. (1971) suggested that DDT and PCB were transported by the atmosphere in different physical states; DDT was carried on dust particles, while PCB were gaseous. These physical states and the non-uniformity of DDT and PCB distributions with depth observed by the present study,

suggested a chlorinated hydrocarbon concentrating mechanism which collected these different physical states unequally. A chlorinated hydrocarbon concentrating mechanism which explained the rapid increase in the DDT content of slick sample #4 and the differing DDT and PCB distributions with depth was the collection mechanism. In this mechanism a transitory slick expanding rapidly over the water surface, driven by winds or spreading pressure, extracted the DDT from dust particles that settled on the water surface and remained there supported by surface tension. This spreading and collecting mechanism accounted for the higher concentrations of DDT found in slicks than in subsurface water, and for the rapid increase of DDT content in surface sample #4. PCB, unreactive with water, and gaseous in the atmosphere would have diffused into the water rather than have built up a high concentration on the water surface. Slick expansion would not have collected many PCB from the water surface and their distribution between surface slick and subsurface water would have been more uniform than the DDT distribution.

The high solubility of chlorinated hydrocarbons in slick material and their low solubility in water made slicks expected collection spots for these pollutants. The different distributions of DDT and PCB found in transitory surface slicks and subsurface water by this study were a result of these chlorinated hydrocarbons being transported in different

states in the atmosphere. A mechanism which explained the distributions observed for transitory slicks was the collection mechanism. Different mechanisms were apparently responsible for the chlorinated hydrocarbon concentrations observed in semi-permanent and transitory slicks. The collection mechanism would not have been as significant in concentrating chlorinated hydrocarbon pesticides for semi-permanent slicks because these slicks were more confined by currents and were not as free to collect pesticides by movements over the water surface. Thus, mechanisms other than the collection mechanism were probably responsible for the high concentrations of chlorinated pesticides found in semi-permanent slicks in the Biscayne Bay, Florida (Seba and Corcoran, 1969). The high concentrations of chlorinated hydrocarbon pesticides they observed in their slicks were not universal, but appeared to be a reflection of the degree and extent of pesticide use in the sample area.

RECOMMENDATIONS FOR FUTURE WORK

Screens, jars, and drum skimmers have been used to sample surface slicks (Garrett, 1965; Seba and Corcoran, 1969; Harvey, 1966). With all of these sampling devices a layer of the surface water is also taken with the surface slick material. A method of determining the relative amounts of water and slick material and contained organics taken in sampling is unavailable. Although these considerations are probably not significant for comparisons of slick studies where results are greatly different, they could be important if results of slick studies are of similar magnitude. The first priorities for any future work in this area should be the development of a surface slick thickness measuring device, the standardization and calibration of sampling techniques, and a method of separation of the surface and dissolved organic fractions.

APPENDIX 1

TABLE 1

SLICK CLASSIFICATION

	Sample #	Date	Classification	Count
1	Surface	Nov. 27,1970	1-Transitory	530
1	Subsurface	Nov. 27,1970	-	156
2	Surface	Nov. 27,1970	3-Transitory	640
2	Subsurface	Nov. 27,1970	-	202
3	Surface	Jan. 30,1971	No Visible Slick	28
3	Subsurface	Jan. 30,1971	-	34
4	Surface	Jan. 30,1971	3-Transitory	256
4	Subsurface	Jan. 30,1971	-	264
5	Surface	Jan. 30,1971	No Visible Slick	338
5	Subsurface	Jan. 30,1971	-	302
8	Surface	Sept. 9,1971	3-Transitory	178
8	Subsurface	Sept. 9,1971	-	108
9	Surface	Sept. 9,1971	2-Transitory	Spilled
9	Subsurface	Sept. 9,1971		86

TABLE 1

(continued)

Sample #	Date	Classification	Count
10 Surface	Sept. 9,1971	2-Transitory	43
10 Subsurface	Sept. 9,1971	-	59
11 Surface	Oct. 5,1971	3-Transitory	120
11 Subsurface	Oct. 5,1971	-	58
12 Surface	Oct. 5,1971	3-Semi-permanent	118
12 Subsurface	Oct. 5,1971	-	152
13 Surface	Nov. 3,1971	3-Semi-permanent	325
13 Subsurface	Nov. 3,1971	-	172
14 Surface	Nov. 3,1971	2-Transitory	208
14 Subsurface	Nov. 3,1971	-	124
Distilled Water Blank			66

The count column above is the total chlorinated hydrocarbon count. This represents the peak heights (in graph units) of all identifiable chlorinated hydrocarbons in the chromatograms.

Samples 6 and 7 were contaminated by lubricant mistakenly applied to the rotary evaporator.

TABLE 2

CONCENTRATIONS

	Sample#	PCB*	Error**	DDT*	Error**
1	Surface	51	±6.8%	17	±5.8%
1	Subsurface	16	"	1	"
2	Surface	37	"	54	"
2	Subsurface	17	"	3	"
3	Surface	2	"	3	"
3	Subsurface	3	"	6	"
4	Surface	21	"	26	"
4	Subsurface	26	"	5	"
5	Surface	33	"	3	"
5	Subsurface	29	"	2	"
8	Surface	12	"	Trace	
8	Subsurface	8	"	Trace	
9	Surface	Spilled	-		-
9	Subsurface	7	"	Not measured	-

TABLE 2

(continued)

Sample #	PCB*	Error**	DDT*	Error**
10 Surface	4	±6.8%	Trace	-
10 Subsurface	5	"	Trace	-
11 Surface	5	"	Trace	-
11 Subsurface	9	"	Trace	-
12 Surface	7	"	12	±5.8%
12 Subsurface	11	"	4	"
13 Surface	24	"	41	"
13 Subsurface	12	"	27	"
14 Surface	13	"	45	"
14 Subsurface	6	"	44	"
Distilled Water Blank	6	"	Trace	

* Concentrations expressed in ppt (parts per trillion weight-weight) or ng./liter.

** These errors represent indeterminate errors.

TABLE 3

ORIGIN OF SLICKS

Sample #	Slick Origin
1 Surface	Unknown
2 Surface	Probably West Point Pulp Mill
3 Surface	No Visible Slick
4 Surface	American Oil Pier (recent origin)
5 Surface	No Visible Slick
8 Surface	Pulp Mill
9 Surface	Pulp Mill
10 Surface	Unknown
11 Surface	Unknown
12 Surface	Mouth of Queen's Creek
13 Surface	Mouth of Queen's Creek
14 Surface	V.I.M.S. Ferry Pier

TABLE 4

AVERAGE CONCENTRATIONS

Slick Type	Average DDT Concentration (parts per trillion)	Average PCB Concentration (parts per trillion)
Transitory Slicks (where DDT Conc. were measurable)	36	31
Subsurface (same samples)	13	16
Semi-permanent Slicks	27	16
Subsurface	16	12

APPENDIX 2

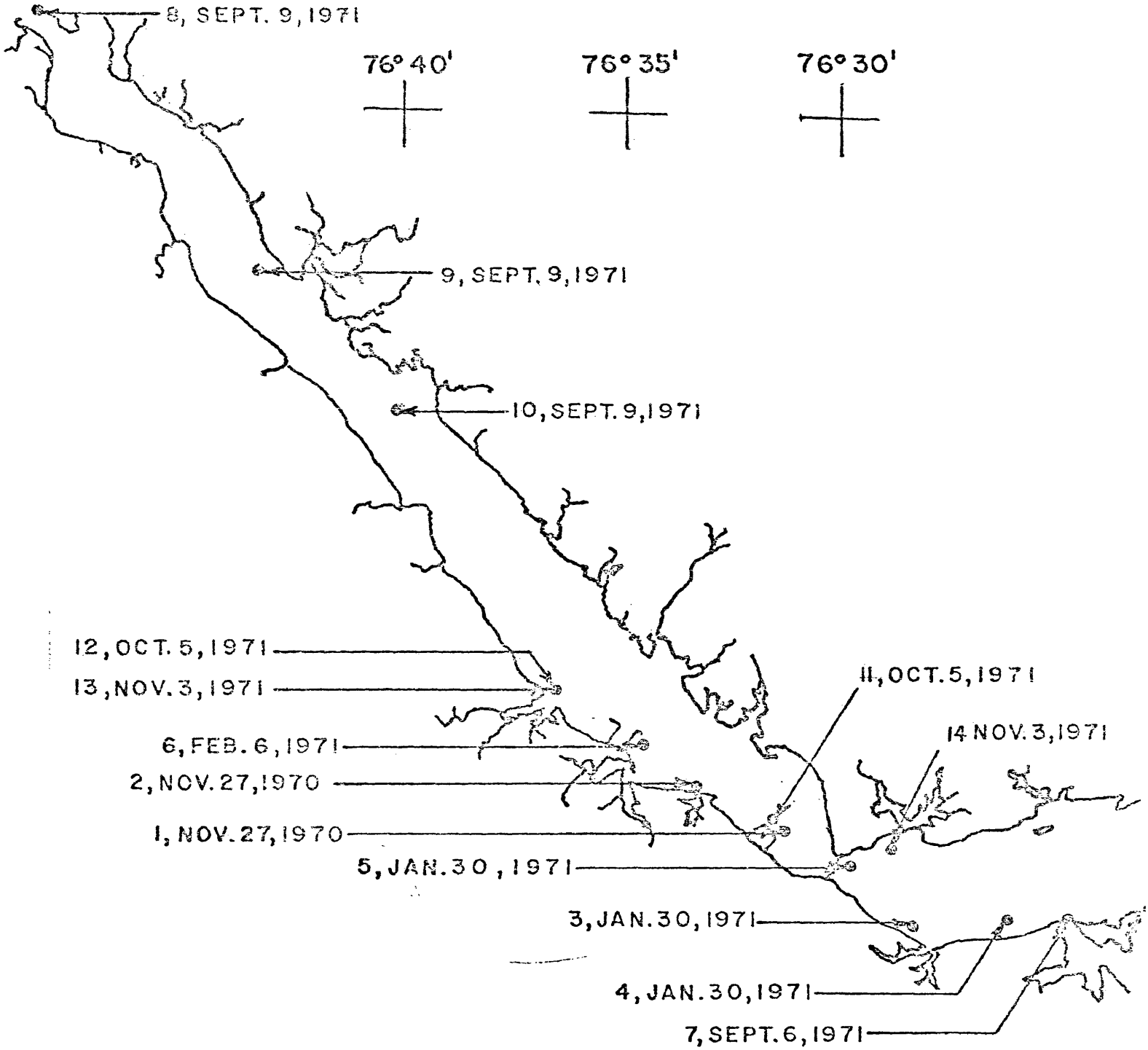

Fig. 1. Sampling locations and dates.

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